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ON THE MECHANISMS OF IONIZATION AND EXCITATION
IN COMETARY ATMOSPHERES

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[Uber die Mechanismen der Ionisation und der Anregung in Kometenatmosphären

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L. Biermann and E. Trefftz

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ON THE MECHANISMS OF IONIZATION AND EXCITATION IN COMETARY ATMOSPHERES

by

L. Biermann and E. Trefftz

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The possible mechanisms for the excitation of the forbidden oxygen lines (aurora lines) in comets are discussed. It is found that the excitation must predominantly take place while the oxygen atom is formed by photodissociation. The total production of suitable parent molecules on the surface of the comet nucleus should be much larger than one would deduct from observations of C_2, CN and CO^+ bands. This high production rate agrees with Whipple's "icy conglomerate model" as applied to 2 recent comets, whose dust production is estimated by Liller. On this basis the local densities of neutral molecules and of electrons and molecular ions formed by photoionization are reexamined as functions of the distance from the cometary nucleus. An estimate is given for the brightness of the comet in the far ultraviolet. The densities are found to be high enough to allow exothermic chemical reactions, especially with molecular ions, up to distances of the order 10,000 km and more. In this way CO^+ especially should be formed. Furthermore the fluctuations in the production of parent molecules will influence the rate of formation of CO^+ molecular ions by way of the chemical reaction, though the time scale of the primary ionization is much longer (> 10 days). Simple model calculations illustrate this last point.

author

1. Introduction

The discovery of the forbidden lines of atomic oxygen in the spectra of a number of comets by Swings and Greenstein (1958; also see Greenstein and Arpigny, 1962) and the more detailed discussion of these observations by Swings (1962) and by Remy-Battiau (1962) are of great significance for the questions of the mechanisms of excitation, chemical changes, and ionization in cometary atmospheres. Because of the slight excitation probability of the [OI] lines, the number of the participating atoms must be large in comparison to the molecules, which contribute the major portion to the luminosity of the body and the tail (CN and C_2; CO^+). This provides a reason for taking up again the question of the amount of gas production of a comet.

In what follows an evaluation will first be made of the quantum emission in the [OI] lines. A discussion of the excitation possibilities which actually exist will then lead to the conclusion that the comet produces very many more molecules containing oxygen than ones which appear in the form of CN and C_2 or CO^+. The resulting rates of production of $\sim 10^8$ gr/sec for medium-bright comets correspond to those which have been found for the dust production of some newer comets (Liller 1960), as Whipple had proposed (1950, 1951) on the basis of his "icy conglomerate model."

If this rate of production is correct from the standpoint of order magnitude, some interesting conclusions are to be drawn. First of all, the total density of gaseous matter in the cometary atmosphere should be higher than has hitherto been assumed. An examination of the prerequisites for chemical reactions leads to the conclusion that, in addition to photochemical reactions, certain exothermic binary reactions, primarily those in which ions participate, could quite probably also occur. In this connection the question of the formation of CO^+ is reexamined; the discussion of a specific model shows that the relatively brief time scales within which existing structures arise from CO^+ in cometary atmospheres may perhaps be understood in this way.

2. The Emission Of The [OI] Lines On Comets

We take the pertinent observation data from the works cited earlier (Swings and Greenstein 1958; Greenstein and Arpigny 1962; Swings 1962). According to them, the occurrence of the red doublet λ6300 + λ6364 and the green line λ5577 is a fairly regular phenomenon; at the same time, the green line may be both stronger and weaker than the red one. Clear-cut cases in which the former was true were presented by the comets 1948 I (Bester) (numerous spectra); 1941 VIII (van Gentt) on June 21-23 and on July 15, 1941, to which, according to Swings (1962) still other cases, not individually specified, of other comets are to be added. The red doublet was certainly present and stronger than λ5577 in the comets 1957 d (Mrkos), 1937 V (Finsler), 1948 XI, 1947 XII (numerous spectra) (at any rate was on a 5577 of similar intensity), 1956 h (Arend-Roland) and 1941 I (Cunningham; observations to some extent dubious). Comparable intensities were observed with the comets 1948 IV (Honda-Bernasconi) and 1957 c (Encke); in addition, Swings lists a number of doubtful cases in which it is difficult to decide what contribution has been made by the sky background.

It is not altogether simple to draw a conclusion from the data in the works cited on the number of quantum transmissions in the total comet atmosphere. The intensity of the green line in the spectrum of the comet 1948 I was usually between those of C_2 emissions (0-1) λ4215 and (0-0) λ5165, and in the spectrum of the comet 1941 VIII even exceeded the intensity of the latter. Hence the emissions must have contributed no altogether small portion to the total light of these comets. There are also similar cases for the red doublet.

Now the number of quantum transitions in C_2 molecules, in the case of medium-bright comets (apparent magnitude +4 at a distance of 1 AU from the Sun and from the Earth), is approximately 10^{32} transitions/sec*).

Hence it appears that we may assume at least about 10^{29} transitions/sec for the [OI] lines, and 10^{30} - 10^{31} transitions/sec in the event of distinct or fairly pronounced appearance of the lines.

Another evaluation which leads to roughly the same results may be arrived at through comparison with the number of transitions per unit area and time which contribute to the luminosity of the night sky. Approximately (1/2 to 1) $\cdot$ 10^9 transitions/cm^{2}sec are necessary for this purpose (Bates 1960); i.e., in cases in which the emission on the comet contrasts sharply with that of the sky background, several 10^9 or 10^{10} transitions/sec must probably be assumed. At the least some 10^{20} cm^2, corresponding to a radius of about 100,000 km, may probably be assigned as the effective cross-section. However, since in many cases the emissions extend far out into the tail, the emitting surface is in individual cases obviously substantially larger still. The combination of these numbers leads again to 10^{29} transitions/sec as a sort of lower limit, i.e., if the emission is recognized clearly as belonging to the comet, and respectively to 10^{30}-10^{31} transitions/sec in the cases in which the emission is distinct or pronounced.

Fig. 1 shows the energy-level diagram of the forbidden oxygen lines. All three terms belong to the basic configuration $2s^2\ 2p^4$. Of importance for the interpretation of these emissions is the fact that the red doublet

*) K. Wurm (1961a) gives $10^{31.8}$ sec^{-1}.

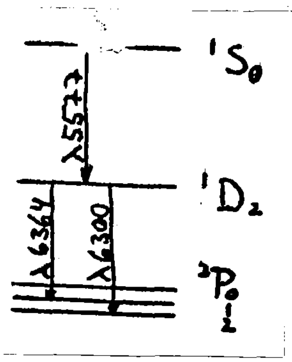

Fig. 1. Energy-level diagram of OI.

arises through transition from the middle term. According to Garstang (1951) the transition probabilities are 0.0091 sec^{-1} for $\lambda 6364$ and $\lambda 6300$, and 1.28 sec^{-1} for $\lambda 5577$.

In the cases in which the green line is markedly more intense than the red lines taken together, the middle term must be depopulated chiefly by other processes within the available period of about 10^2 sec.

3. Excitation Mechanisms Of The [OI] Lines.

Basically we have the following possibilities for interpretation of the [OI] lines, i.e., excitation of the upper levels:

(1) Radiation excitation

(2) Collision excitation by electrons

(3) Dissociative recombination

(4) Photodissociation.

The first possibility is virtually excluded because of the required quantities of neutral oxygen and for still other reasons (Swings 1962).

The possibilities of collision excitation have already been examined by Remy-Battiau (1962), among other things from the standpoint of whether there is any combination of electron temperature (T_e) and electron density (n_e) which would make clear the predominating intensity of the green line $\lambda 5577$. The latter is not the case. The excitation probability of the ^1D state for electron temperatures of $\gtrsim 10^4$ degrees is $0.4 \cdot 10^{-9}$ $cm^3 sec^{-1}$ n_e (Seaton 1958a). Hence an average electron density of, say, 10^4 cm^{-3} would yield an excitation probability of $4 \cdot 10^{-6}$ sec^{-1} per OI atom. We shall return later to the probable values of n_e; at any rate, with the values assumed here, $\sim 1/4 \cdot 10^{35}$ to 10^{36} OI atoms would have to be present.

If we assume that the O atoms contribute to the visible emission up to a distance of $\sim$100,000 km from the nucleus, i.e., with a velocity of 1 km/sec over $\sim 10^5$ sec (cf. Section 3), this corresponds to a production rate of some 10^{29} to around 10^{31} sec^{-1}.

Of interest in this connection is the observation datum that the intensity decrease of the [OI] lines is weaker than for any neutral molecule. Since the product of the density of both partners enters into collision processes, generally speaking a more rapid decrease in emission outwards should be expected than in processes based on radiation excitation. The emissions of the C_2 molecules, however, which contribute the major portion to light in the visible region (Swings and Hasser, Atlas of Repr. Com. Sp.), are based on radiation excitation. According to the observations of F. Miller (1961), the intensity decrease in C_2 at a distance of some 10,000 km from the nucleus corresponds to a density decrease proportional to $1/r^2$, but at a greater distance rather to such a decrease proportional to $1/r^3$. Hence these observations do not indicate that electron collision excitation contributes appreciably to luminosity in the [OI] lines, although a participation of electron collisions in the formation of the [OI] lines is naturally not to be excluded. In addition, the conditions may vary rather widely from comet to comet.

The other two mechanisms have been widely discussed in connection with the corresponding formulations of the problems for the aurora borealis and night sky luminosity. Dissociative recombination, i.e., the process

$$AB^+ + e \longrightarrow A + B$$

has very high cross-sections for many molecule ions; the reaction rates are then $> 10^{-8}$ cm^3 sec^{-1}, and in the case of O_2^+ even $\gtrsim 10^{-7}$ cm^3 sec^{-1} (Bates and Dalgarno 1962). Since usually more ionization energy is gained than dissociation energy is required, some energy remains (3 - 5 ev in typical cases, but 7 ev and 9 ev respectively in the case of O_2^+ and H_2^+ - OH^+) and quite probably is used for excitation of one of the neutral atoms formed. Hence the mechanism is plausible as such, insofar as the observed decrease in density (vide supra) can be interpreted. However, a considerable limitation results from the fact that it must have been preceded by an ionization of the molecule; under the given conditions, primarily photoionization through the ultraviolet radiation of the sun is suitable for the purpose. According to the latest measurements by Hinteregger and Watanabe (1962), the photon flow with $\lambda < 1025$ Å, the ionization boundary of O_2, is $\sim 6 \cdot 10^{10}$ cm^{-2} sec^{-1} in the vicinity of the earth. The resulting ionization probabilities are of the order of 10^{-6} sec^{-1}. Several examples are given in Table 1.

Table 1. Photoionization and Photodissociation Probabilities.

Molecule	Ionization [sec^{-1}]	Dissociation [sec^{-1}]
CH_4	$6 \cdot 10^{-7}$	$5 \cdot 10^{-6}$
NH_3	$8 \cdot 10^{-7}$	$4 \cdot 10^{-7}$
H_2O	$5 \cdot 10^{-7}$	$2 \cdot 10^{-5}$ *)
O_2	$5 \cdot 10^{-7}$	$5 \cdot 10^{-6}$

*)With a private communication from Dr. Tousey taken into account, a dissociation probability of 1×10^{-5} sec^{-1} is obtained.

The numerical values in Table 1 were estimated from the data of Nicolet (1961) and the tables of Hinteregger (1961). With allowance made for more recent measurements, the values could still be changed somewhat, by a factor roughly of up to 2 (Detwiler and co-workers 1961; in addition, we are extremely grateful to Dr. Tousey for the communication of more recent results).

The process discussed in earlier works (Biermann 1953, Cherednichenko

1959/1960) of ionization by molecules through charge transfer in the solar wind has been rendered more improbable by the latest measurements. According to it the proton flux in interplanetary space under fairly calm conditions amounts to some 10^8 particles/cm^2 sec (Snyder 1963). With a charge transfer cross-section of about 10^{-15} cm^2 the ionization probability due to charge exchange would thus be some 10^{-7} sec^{-1}.

In addition to dissociative recombination, charge transfer processes occur between comet ions and molecules in an only partly ionized gas, processes in which primarily ions with a lower ionization potential arise, e.g., $N_2^+ + X \rightarrow N_2 + X^+$ (N_2 with 15.6 ev has a particularly high ionization potential, so that almost every such reaction is exothermic).

Lastly, exothermic reactions between ions and non-ionized atoms and molecules in which neutral O atoms, among others, may arise, must also be taken into account. An example of this possibility is provided by $N + O_2^+ \rightarrow NO^+ + O + 4.3$ ev.

Like photoionization, photodissociation is also limited by the ultraviolet intensity of the sun. Because of the wavelength dependence of the dissociation cross-section, in most cases it also leaves enough excess energy so that one of the arising atoms may be formed as an excited one. A typical example is the photodissociation of O_2: while in the region of the Herzberg continuum (λ 2400 - 1750 Å), which corresponds to dissociation in two oxygen atoms in the state with the lowest energy, the absorption cross-section is quite small, this cross-section is in the region of the Schumann continuum ($\lambda < 1750$ Å) so much larger (maximum value nearly 2×10^{-17} cm^2 with λ1500 - 1400 Å) that the intensity decrease in the continuous spectrum of the sun is far overcompensated. In this instance the O_2 molecule dissociates into an O atom in the ground state and one in the ^1D

state (Herzberg 1950). Although a part of the absorption processes does not lead to dissociation, the probability that upon the photodissociation of O_2 in undiluted sunlight at least one of the atoms arises in the excited state is surely of the first order. Of course, the data on the absorption cross-sections do not suffice to permit a statement as to the probability with which the more highly excited state ^1S is reached. O_2 is admittedly not one of the oxygen compounds which one would expect to occur with any great frequency on comets. However, its behavior is typical of many molecules. Generally speaking dissociating states leading to atoms in the ground state differ from the deepest bound state in their total spin. A transition from the ground state to these states is thus optically forbidden. The first optically permitted transition to a dissociating state leads to at least one excited atom. In the final analysis, for a diatomic molecule photodissociation with subsequent dissociative recombination is naturally exactly equivalent to photodissociation.

The dissociation probabilities for molecules in sunlight are generally somewhat higher than the ionization probabilities; examples are given in Table 1.

However, our knowledge of the absorption cross-section scarcely suffices for a decision as to whether a distinct preference for the mechanism of photodissociation with regard to interpretation of the [OI] lines follows from this. It is rather the observation data of the slight intensity gradients which make it probable that photodissociation generally yields the excited O atoms.

Observations and considerations of plausibility suggest the assumption that the neutral molecules flow outward from the cometary nucleus at a velocity v_{mol} of the order of magnitude of 1 km/sec (see Section 7 for the velocities in the vicinity of the nucleus). Hence they will reach a distance from the nucleus of 100,000 km in about 10^5 sec. This means that a suitable parent molecule will on the average participate once at the most in one of the processes which lead to emission of a quantum in one of rht [OI] lines. In many cases, however, the emission will disappear in the sky background because the distance from the nucleus is too great. The figures cited above for the frequency of quantum transitions should thus represent the lower limits for the evaporation of suitable molecules on the surface of the comet. If Q is the number of particles leaving the cometary nucleus per unit time and solid angle, for bodies in the case of which the [OI] lines still barely contrast with the sky background Q definitely must be greater than 10^{28} sec^{-1}, and for distinctly contrasting [OI] lines Q must even be larger than 10^{30} sec^{-1}.

4. The Special Case $\lambda 5577$ Bright Against ($\lambda 6300$ + $\lambda 6364$)

The difficulty of interpreting this phenomenon lies in the brevity, already emphasized, of the period of only about 10^2 sec within which the de-excitation from the intermediate state ^1D must take place; in cases in which the green line clearly predominates, the de-excitation time may even be only of the order of 10^1 sec, at the maximum.

It has already been mentioned that a predominant excitation through electron collisions would not, according to the results of the investigation of Remy-Battiau, explain these cases. One conceivable alternative, that of two quantum transitions between the states ^1D and ^3P is likewise excluded, since these transitions are doubly forbidden.

The only possibility of understanding these cases appears to lie in attainment of the ^1S state through photodissociation or dissociative recombination, while the de-excitation of the ^1D state results from collisions of electrons the mean energy of which lies only in the range of

1 - 2 volts, so that collision excitation of the upper state may be left out of consideration. The probability of excitation from the ^1D state in the temperature range in question (10^4 °K) is about 7×10^{-9} cm^3 sec^{-1} according to Seaton (1958a); hence deexcitation in 10^2 or 10^1 sec requires electron densities of easily 10^6 or 10^7 cm^{-3}. These electron densities are higher in order of magnitude than would be assumed on the basis of all other data. In the Earth's atmosphere, which we shall cite for the sake of comparison, the emission of the green line predominates in night sky luminosity at altitudes lower than about 120 km (Seaton 1958b) (lower limit of the emission at approximately 100 km). At these altitudes the total particle density decreases from about 10^{13} to 10^{12} cm^{-3}, and that of molecular oxygen more sharply, since photodissociation makes itself felt to an increasing extent at 100 km and above.*)

The depopulation of the ^1D level is brought about here by collisions with neutral molecules. The ratio of the intensity of the red doublet to that of the green line was explained by Seaton (1958b) by reaction rates of 2×10^{-11} cm^3/sec for resonance collisions with O_2 and by 3×10^{-14} cm^3/sec for any other collisions (predominantly with N_2). The electron density of less than 10^5 cm^{-3} is too low at these altitudes to explain the phenomenon.

There do not appear to be any competitive processes with a higher reaction rate; at least, the authors have not succeeded in finding any. Of course, it must be admitted that not enough is known about the corresponding figures, say for collisions of O atoms in the ^1D state with molecules, or reactions with molecules (still to be discussed), to permit a definitive decision in this question.

*)For the latest data see, for example, R. A. Hord (1962).

Hence it appears that we have only the following alternatives: either special circumstances play a more important part in the case of the not too numerous comets in which the green line has been found in predominating intensity than has hitherto been perceptible from the observation data (with the 1948 I comets, for example, the emission extended exceptionally into the tail, but with a distribution entirely different from the emission of CO^+), or the gas densities in these cases are still somewhat higher than discussed here, so that the conditions become more like those in the corresponding layers of the Earth's atmosphere.

5. Density Distribution And Temperature of Electrons In The Coma

At this point let us take up the role of electrons again. Free electrons arise inside the head of the comet, predominantly, it is assumed, by photoionization. If the molecule density is given by

$$n_{mol}(r) = \frac{Q}{v_{mol}\, r^2} \tag{1}$$

then the electron density n_e in the outer regions of the cometary atmosphere, insofar as they are optically thin to ionizing radiation, is in approximation

$$n_e(r) = \frac{Q}{v_{mol}\, r} \cdot \frac{\alpha_i}{v_{pl}} \tag{2}$$

α_i = ionization probability.

A distinction is made here between the velocity v_{mol} of the neutral molecules and the (radial) velocity v_{pl} of the ions, which latter is still to be discussed at the end of this section. We may set $v_{pl} \approx v_{mol}$ for small distances from the cometary nucleus. n_e (r) does not increase randomly toward the interior, since the ionizing radiation is screened out there; it has a maximum at an optical thickness in the vicinity of $\tau \approx 1$. If we assume an absorption cross-section of $\sigma \approx 10^{-17}$ cm^2, the radius of maximum electron density is calculated from

$$\int_{r_{\tau=1}}^{\infty} n_{mol}(r)\,dr = \frac{Q}{v_{mol}\, r_{\tau=1}} \approx \frac{1}{\sigma} = 10^{+17}\ cm^{-2} \qquad (3)$$

with $Q/v_{mol} = 10^{25}$ molecules per solid angle and cm along r (see Section 3), $r_{\tau=1} = 1{,}000$ km. The electron density at this point should amount to approximately

$$n_e(r_{\tau=1}) \approx \frac{Q}{v_{mol}\, r_{\tau=1}} \cdot \frac{\alpha_i}{v_{pl}} \approx 10^{17}\ cm^{-2} \cdot \frac{\alpha_i}{v_{pl}} \approx \frac{1}{2} \cdot 10^{6}\ cm^{-3} \qquad (4)$$

According to Table 1, $\alpha_i \approx 1/2 \times 10^{-6}$ sec^{-1}; 1 km/sec is assumed for v_{pl}. Equation (4) gives an upper limit for electron density, independently of the production Q of the comet.

The wavelength dependence of the ionization cross-sections together with the ultraviolet radiation of the sun has the result that the electrons are first released with an average kinetic energy of more than 10 ev. This high energy value is explained largely by the strong radiation intensity of the sun in the He I resonance line at 584 Å and the He II Ly α line at 304 Å. Heat exchange of the electrons among themselves chiefly competes with cooling through inelastic collision processes. The rate of elastic momentum compensation of the electrons among themselves is about 2×10^{-6} cm^3/sec.*)

At a density of 10^4 electrons/cm^3 this leads to a time scale of ~50 sec ≈ 1 min prior to cessation of a Maxwellian velocity distribution.

At first, i.e., so long as the energy of the electrons is $\gtrsim 5$ ev, the cooling is effected by excitation of higher electron states, dissociation, and ionization of the molecules. If we assume a cross-section of about 10^{-17} cm^2 for these processes, the cooling rate is $\sim 2 \times 10^{-9}$ cm^3/sec. The latter is to be multiplied by the molecule density to obtain the time scale of the cooling.

*)See, for example, R. Luest, F. Meyer, E. Trefftz, L. Biermann (1962).

If, as above, we assume a production Q of the cometary nucleus such that $Q/v_{mol} \approx 10^{25}$ molecules per cm and solid angle, the cooling takes several minutes at a distance of some 10,000 km from the nucleus ($n_{mol} \approx 10^6 + 10^7$ cm^{-3}). For lower electron energies ($\lesssim 5$ ev), vibration, and ultimately rotation excitation of molecules have large cross-sections (up to some 10^{-16} cm^2), so that the cooling should proceed even more rapidly in this region.

For energy reasons each electron can accomplish only 1 to 2 collisions of the first kind (electron excitation, dissociation, ionization). Since the number of electrons in the head of the comet depends on the effectiveness of photoionization by the sun, electron collision processes are to be ignored in favor of photo processes to the extent that the radiation intensity of the sun which causes the ionization is small in comparison to that which causes the process under consideration, e.g., excitation (due allowance being made for the oscillator strengths of the processes). This makes it clear that electron collision processes are of no importance for excitations in the visible regions, regardless of any assumptions as to the densities.

For vibration excitation the collision cross-sections are essential only for energies between about 5 to 10 vibration quanta (G. J. Schulz 1962; A. Herzenberg, F. Mandl 1962). Since on the average 2 to 3 quanta are excited per collision, in this case as well each electron can accomplish only about 2 collisions before its energy becomes too low for this excitation. Excitation of the forbidden oxygen levels falls in the same energy region. The electron collision cross-sections for this purpose are smaller than those for vibration excitation. Hence of the available electrons, which are few to begin with, the majority are cooled to energies below 2 ev, without having excited an oxygen atom to a forbidden transition.

The density of the electrons is further limited by dissociative recombination. If we consider for a molecule class j the equilibrium between photoionization (probability α_i^j), dissociative recombination (recombination rate γ_j (cm^3/sec)) and outflow (molecular velocity v_{mol}, ionic velocity v_{pl}), the ion density is proportional to r^{-1}: For

$$N_j(r) = r^2 n_j(r) \qquad (N_j \text{ ion density per solid angle and cm along } r) \tag{5}$$

the differential equation

$$v_{pl} \frac{dN_j}{dr} = - N_j n_e \gamma_j + \frac{Q_j}{v_{mol}} \alpha_i^j \tag{6}$$

is valid; Q_j = production per solid angle and sec for the neutral molecule j; $n_e = \Sigma n_j$ is the electron density. The equation is solved by

$$N_j(r) = a_j r \quad \text{and} \quad n_j(r) = a_j / r \quad \text{respectively,} \tag{7}$$

with

$$a_j = \frac{\alpha_i^j Q_j}{v_{mol}} \cdot \frac{1}{v_{pl} + \gamma_j \sum_k a_k} \tag{8}$$

There follow

$$a_j < \sqrt{\frac{\alpha_i^j Q_j}{\gamma_j v_{mol}}} \quad \text{and} \quad a_j < \frac{\alpha_i^j Q_j}{v_{mol} v_{pl}} \tag{9a,b}$$

For an ion class with high dissociative recombination, say $\gamma_j = 10^{-7}$ cm^3/sec, the first condition (assuming $\alpha_i^j = 1/2 \times 10^{-6}$ sec^{-1}) yields

$$n_j < 0.7 \cdot 10^4 \text{cm}^{-3} \times \frac{10\,000 \text{ km}}{r} \times \sqrt{\frac{Q_j/v_{mol}}{10^{25} \text{cm}^{-1}}} \tag{10}$$

The electrons are yielded primarily by molecules whose dissociative recombination rate is small. Then, with the values of Q and v assumed in this paper, the second of the inequalities given above is generally the decisive one, specifically, as soon as

$$\frac{\dot{\alpha}_i^j\, Q_j\, \gamma_j}{v_{mol}\, v_{pe}^2} < 1 \qquad (11)$$

approximately when $\gamma_j \lesssim 10^{-8}$ cm^3 sec^{-1}. That is to say, the electron density is determined under these conditions by the outflow velocity and not by dissociative recombination.

Lastly, let us estimate the influence of the electrons on the plasma velocity. If we assume that the kinetic temperature of the electrons in equilibrium with the ions balances out at about 1 ev, the isothermal acoustic velocity in the plasma is about 3 km/sec (the mean molecular weight being assumed as 10). For the outflow velocity of the plasma we generally have a small multiple of the isothermal acoustic velocity, about 10 km/sec at a distance of some 10,000 km from the nucleus. Hence it is 1/2 to 1 order of magnitude higher than the velocity of the neutral gas. A prerequisite for this consideration is that the Debye length l_D be small in comparison to the dimension of the comet, it being satisfactorily met in this case by $l_D \approx 10$ cm.*)

6. The Gas Production Of Comets

We shall compare the figures found for gas production first with data of a different origin, primarily with mass losses in the form of dust. The latter were investigated by W. Liller (1960) for the Arend-Roland 1956h and Mrkos 1957d comets, both of which showed the red doublet distinctly. Liller found values of 0.9 and $2 \cdot 10^{14}$ for the total mass of the dust which at a certain moment contributed to the visible dust tail, and a mass loss of 0.8×10^8 and 1×10^9 gr/sec, allowing for the acceleration by light pressure. A mass loss of 10^{31} mol/sec from the mean molecular weight of 20 would correspond to 3×10^8 gr/sec. According to the "icy conglomerate

*) $l_D = 6.9\,\mathrm{cm}\sqrt{\frac{T_e/°K}{n_e/\mathrm{cm}^3}}$ See, for example, L. Spitzer (1956).

model" conceptions of Whipple (1950, 1951), the total mass of the molecules, present as ice, should above all be comparable to the hydrogen compounds of oxygen, nitrogen, and carbon or be a small multiple of the mass of dust matter. Hence the high frequency here postulated of hitherto unobserved gases in the cometary atmosphere agrees with Whipple's theory. Similarly, the total masses are compatible with those estimated from the lifetime and probable diameter of the solid nucleus: If a comet over a period of about 10^9 sec on an average loses 10^9 gr/sec in each case in the vicinity of the sun (Liller 1960), this would correspond to a total loss of 10^{18} before its complete disintegration; on the other hand, the total volume of a comet with an (initial) radius of 10 km would be $10^{18.6}$ cm^3.

The general question of whether it is probable that the neutral molecules such as CH_4, C_2H_4 ...., NH_3 ...., H_2O, CO_2 HCN, etc., which cannot be observed from the surface of the Earth, predominate in comparison to the mass of those which are in evidence in the spectra of the head and tail has been repeatedly discussed. Poloskow (1957) finds that the presence or absence of other molecules cannot be concluded from the observable spectra. The molecules referred to above have in the visible portion only bands which correspond to transitions between excited levels. In the cometary atmosphere, however, only excitation of resonance bands from the ground state is to be expected. Generally speaking, this is based on the circumstance that the dilution factor of solar radiation amounts to about 10^{-5} at a distance of 1 AU in interplanetary space, so that excited states (except for ones in which special conditions are present) should generally be underpopulated in comparison to the population to be expected in the solar atmosphere.

A fact of interest in connection with the question of the total density of gaseous matter in cometary atmospheres is that the temperature derived from the population of the vibrational states of the symmetrical C_2 molecule is of the order of several thousand degrees, while the corresponding temperatures for CN and CO^+ are far lower (WURM 1959). Unfortunately, for the time being the data which would be required for a quantitative interpretation of this observation are still lacking. Furthermore, the total gas production must be greater than that which leads in one of the ways discussed to the emission of the [OI] lines. It may also be safely assumed that the gas production will vary considerably from comet to comet and with changing distance from the Sun. If an unvarying production $Q = 10^{30}$ particles/sec x solid angle is taken as a basis for the following discussion, this is done merely for the sake of not having always to introduce a correspondingly wide margin; the influence of the dependence on the actual production may be seen with no difficulty. The roughly circular shape of the coma in the emissions of neutral molecules suggests the assumption that the production of gas from the surface proceeds isotropically in the first approximation, probably in consequence of sufficiently rapid rotation.

7. Density And Temperature Distribution Of Molecules In The Coma.

With the density distribution, equation (1),

$$n_{mol}(r) = \frac{Q}{v_{mol}\, r^2} = \frac{10^{25}\,cm^{-1}}{r^2} \qquad (1b)$$

the following is obtained for the number of molecules along a visual ray passing the cometary nucleus at a distance s:

$$\mathcal{N}_{mol}(s) = \pi s\, n_{mol}(s) = \frac{10^{25.5}\,cm^{-1\,*)}}{s} \qquad (12)$$

---

*)For more complicated density distributions L. Haser (1957) gives the expression for the number of particles along a visual ray.

Most molecules are subject to dissociation in sunlight. For CH_4, H_2O, and others the first dissociation depends on the intensity in Ly α. If we assume a dissociation probability $\alpha_d = 10^{-5}$ sec^{-1} (see Table 1), the density of atomic hydrogen, provided that subsequent reactions could be ignored, would be

$$n_H(r) = \frac{Q\,\alpha_d}{v_{mol}^2\, r} \approx 10^6 \text{ cm}^{-3} \times \frac{10\,000 \text{ km}}{r}$$

This formula is valid for 1,000 km $\lesssim$ r $\lesssim$ 50,000 km. Below r = 1,000 km the dissociating radiation is screened out, i.e., the optical thickness of the layer above is > 1. Extinction of the parent molecules becomes noticeable above 50,000 km. The observations even suggest that a large portion of the dissociations is virtually completed even at 10,000 km (Miller 1961, Wurm 1961b). At distances of the order of 100,000 km a part of the molecules such as CH_4 would already be dissociated several times. The higher temperatures of the resulting free atoms -- kT at first several ev -- is a source of heat for the atmosphere. (For optical thickness in Ly α, see the next section).

It is useful for the following discussions to visualize the layers of the Earth's atmosphere to which the cometary atmosphere corresponds with respect to the influence of the ultraviolet radiation of the Sun. The total thickness of the Earth's atmosphere above the level with pressure p (dyn/cm^2) is about 2.0 x 10^{19} x p molecules/cm^2. If we assume the radius of the cometary nucleus as being 10 km, over the surface of the latter there are 10^{19} molecules/cm^2, which on Earth correspond to p $\approx$ 1/2 dyn/cm^2, that is, fairly exactly to the 100 km level of the Earth's atmosphere (Hord 1962). The number of molecules above a certain level in the cometary atmosphere, again if we at first disregard the influence of dissociation, decreases inversely to the first power of the distance from the cometary nucleus. As regards the decisive absorption cross-sections for ultraviolet radiation, reference may be made, for example, to Nicolet's representation (1961). Hence the layers of the terrestrial "thermosphere" or "chemosphere" whose lower boundary is assumed to be between about 90 and 100 km and in which the temperature rises with increasing altitude from about 200 to about 1,500 $^{\circ}$K, would correspond to the distance between 10 and 1,000 km from the cometary nucleus. The upper boundary corresponds only to $\sim 10^{17}$ molecules/cm^2; above it only certain spectral regions are partially absorbed, but not completely extinguished. Consequently, despite the differences in chemical composition, one may safely assume that heating by the ultraviolet radiation of the Sun plays an essential role in the cometary atmosphere and that kinetic temperatures of the order of 1,000 - 2,000 $^{\circ}$K are to be regarded as normal for neutral gas. Of course, the result of the difference in the available time scale -- only 20,000 km corresponds at 1 km/sec to about one-fourth of a day, while the time scale for the absorption of sunlight is of the order of one day -- is that the "thermosphere" of the comet must be far more extensive. Furthermore, it is reasonable to question the extent to which the structure of the cometary atmosphere can be described by equations after the analogy of those which have been discussed by Parker (1961, 1963) in connection with the theory of the continuous components of solar corpuscular radiation ("solar wind"). An essential difference naturally lies in the circumstance that on the comet the acoustic velocity of the matter evaporated on the surface is large in comparison to the escape velocity, which is determined by the gravitation potential of the comet. One would accordingly expect a velocity which is of the order of the acoustic velocity, but not a large multiple of it, and which increases slightly toward the exterior.

The acoustic velocity, as well as the temperatures, increase toward the exterior. Because of the asymmetry of irradiation of the cometary surface and the other unknowns, the comparison can scarcely be carried further, except that it may perhaps be stated that the ratio of the observable outflow velocity to the probable value of the isothermic acoustic velocity on the surface proper of the comet (several m/sec according to Donn and Urey (1957)) appears reasonable. If one follows Donn and Urey and assumes a temperature of 150 °K on the cometary surface, the pressure on the cometary surface would be of the order of magnitude of 10^{-1} - 1 dyn/cm^2 and the decrease outwards would correspond to the pattern of density, temperature, and molecular weight.

8. Resonance Fluorescence Radiation In The Far Ultraviolet

Lastly, it is of interest to estimate the luminosity of a comet in the ultraviolet region. If we assume a molecule whose partial density is comparable to the total density here assumed, the fact must be taken into account that the comet becomes optically dense in its interior. We shall first estimate the optical cross-section σ of a molecule. It is

$$\sigma = 4\pi\alpha\pi a_0^2 \times f \times (\Delta V / R_y)^{-1} \tag{13}$$

where $4\pi\alpha\pi a_o^2 = 0.8 \quad 10^{-17}$ cm^2 (α, fine structure constant; a_o, Bohr radius), f is the oscillator strength and $\Delta V/Ry$ the width of the line in Rydberg units. For f we must introduce the oscillator strength of an individual rotation line f_{rot}. For ΔV we take the Doppler width at a kinetic energy of 3 to 4 ev and a molecular weight of about 20. If we set

$$f_{rot} = 10^{-3} \qquad \Delta V / R_y = 10^{-5}$$

then

$$\sigma \approx 10^{-15} \text{ cm}^2 \tag{13a}$$

If we now assume, as above, that the molecule density is given by equation

(1) with $Q/v_{mol} = 10^{25}$ cm^{-1}, according to (3) the radius over which the matter has the optical thickness $\tau \approx 1$ is

$$r_{\tau=1} \approx 100\ 000 \text{ km}$$

The optical thickness along a visual ray at distance $r_{\tau=1}$ from the nucleus is then π (cf. equation (12)). It decreases as r^{-1} outwards. If R is the radius up to which the cometary radiation is visible, the effective area for the absorption of sunlight is

$$\pi R^2 \bar{\tau} \approx \pi R^2\, 2\tau(R) \quad \text{if} \quad \tau(R) \ll 1 \tag{14a}$$

or

$$\pi R^2 \bar{\tau} \approx \pi R^2 \quad \text{if} \quad R \approx r_{\tau=1} \tag{14b}$$

$$\pi R^2 \bar{\tau} \approx 10^{21} \text{ cm}^2$$

follows for $R \gtrsim 100{,}000$ km.

Lastly, we must also estimate the portion of the spectrum which is absorbed in the individual lines of a band. According to the above estimates, the Doppler width at 2,000 Å is about 0.04 Å. If we assume a mean distance of the rotation lines of 0.2 Å, the spectral utilization of sunlight is

$$a \approx 0.2.$$

If $\lambda \approx 2{,}000$ Å, one may assume (Hinteregger 1962) that the sun radiates about

$$\Phi_{bands} \approx \frac{\text{photons}}{\text{cm}^2 \text{ sec}} \tag{15a}$$

in the region of a band of a width of about 5 - 10 Å (i.e., 25 - 50 rotation lines) onto the comet, of which

$$a\Phi_{bands} \approx 10^{11.3} \frac{\text{photons}}{\text{cm}^2 \text{ sec}} \tag{15b}$$

are absorbed. Then according to equations (14b) and (15b) the total radiation of the comet is

$$10^{32.3} \frac{\text{photons}}{\text{sec}},$$

hence somewhat more than in the visible region. Assuming a distance of 1

AU between the Earth and the comet, there would be about

$$10^5 \frac{\text{photons}}{\text{sec cm}^2}$$

to measure in this case. This is approximately as much as the flow measured in this wavelength region ($\sim 2{,}000$ Å)(Alexander, Bowen, Heddle 1963, bandwidth ~ 300 Å). Since presumably several bands in the ultraviolet contribute to the radiation of the comet, it should be possible to determine by rocket measurements if the densities assumed here are the actual ones. Since atomic hydrogen as well is to be expected with fairly great frequency as a dissociation product, a corresponding flow should also be observable in Ly α, etc. The energy flow in Ly β should lead to transitions to the third quantum orbit of the HI and to emission in about one-eighth of the cases. However, the flow in Ly β in the solar spectrum is only $\sim 1/100$ that in Ly α (Hinteregger 1961). As regards the emission, otherwise unexplained by F. D. Miller (1962), which was observed in the vicinity of Hα in the spectrum of the comet 1955e (Mrkos), an evaluation of the intensity to be expected is of interest.

First of all, it is clear the radiation pressure on HI atoms is not altogether small. The quantum flow per frequency unit in Ly α amounts to $H_\nu/h\nu \approx 0.2$ cm^{-2} (the effective line width being assumed as 1 Å); thus we obtain from the oscillator strength (0.42) (Unsoeld 1955)

$$\frac{H_\nu}{h\nu} \cdot \frac{\pi e^2}{mc} \cdot f = 10^{-2.6} \text{ sec}^{-1} \tag{16}$$

transitions per H atom in which an impulse of $h\nu/c = 10^{-21.2}$ g cm/sec is received. The resulting acceleration is 0.8 cm/sec^2, so that a distance from the nucleus of $4 \cdot 10^6$ km is reached in 10^6 sec. A quantum flow in Ly α of barely $4 \cdot 10^{11}$ cm^{-2} sec^{-1} is assumed here (Detwiler, Garret, Purcell, Tousey 1961).

If we calculate the effective optical cross-section for the Lyman lines in accordance with equation (13), the Doppler width for several ev of kinetic energy being introduced for $\Delta\nu$, we obtain

$$\sigma(Ly\,\alpha) \approx \tfrac{1}{2}\cdot 10^{-13}\ \mathrm{cm}^2$$

and

$$\sigma(Ly\,\beta) \approx 10^{-14}\ \mathrm{cm}^2$$

With the particle density assumed above of $Q/v_{mol} \approx 10^{25}$ particles per solid angle and cm along r, the radius r over which lies a layer of matter of optical thickness 1 would be greater than 10^6 km. In this case, however, the radius is determined by other quantities, such as the lifetime of the H atoms versus photoionization ($\sim 10^{-7}$ sec^{-1}) and external influences (e.g., charge transfer in the solar wind). We adopt $R = 10^6$ km, $\overline{\tau} = 1$; hence

$$\pi R^2 \tau = 10^{22.5}\ \mathrm{cm}^2$$

The spectral utilization of sunlight should amount to about

$$a \approx 0.1$$

($\Delta\lambda$ (comet) ≈ 0.1 Å versus 1 Å width of the solar line). A solar emission in Ly α of about $4 \cdot 10^{11}$ photons/cm^2 yields a cometary radiation of

$$10^{33}\ \frac{\text{photons}}{\text{sec}}\ \text{in Ly}\ \alpha. \tag{17a}$$

In Ly β the quantum flow of the sun is barely 1/100 that in Ly α. The total radiation of the comet amounts to

$$10^{31}\ \frac{\text{photons}}{\text{sec}}\ \text{in Ly}\ \beta. \tag{17b}$$

At a distance of 1 AU from the comet this is

$$10^{5.5}\ \frac{\text{photons}}{\text{cm}^2\ \text{sec}}\ \text{and}\ 10^{3.5}\ \frac{\text{photons}}{\text{cm}^2\ \text{sec}}\ \text{in Ly}\ \beta \tag{18a,b}$$

About 1/8 of the transitions from the third quantum state leads to emission of Hα. Altogether, then, this is

$$10^{30}\ \frac{\text{photons}}{\text{sec}}\ \text{in H}\alpha, \tag{19}$$

i.e., 2 tenth powers less than, for example, in the Swan bands (Wurm 1963).

An evaluation of the Ly α radiation with densities such as have been found for visually observed molecules leads to a radiation of $\sim 10^{30.5}$ ph/sec. Proof of it probably lies beyond the bounds of technical feasibility for the time being.

9. Collision Processes, Including Charge Transfer And Chemical Reactions

The free path length against ordinary gas-kinetic collisions is, according to the kinetic theory of gases, about $(10^{-14}\ cm^2 \cdot n)^{-1}$ (n = particle density) for H_2O or CO_2 at 300° K; hence when $r < 10^{11}$ cm it should be smaller than the distance from the nucleus. Of course, the fact must be taken into account that with outflow energy of random motion is continually transformed into energy of oriented motion; on the other hand, heat is constant supplied, so that without more detailed analysis it cannot be stated which of the two effects predominates. At any rate, hydrodynamic laws may safely be applied in the regions in question up to a distance of some 100,000 km from the cometary nucleus.

Now we shall consider the role of chemical reactions. Exothermic binary reactions, in which an ion reacts with a neutral atom or molecule and whose activation energy is small, have the highest probabilities (measured by the reaction rate γ_{chem} ($cm^3\ sec^{-1}$)). In these cases the reaction rate is of the order of 10^{-9} to 10^{-8} $cm^3\ sec^{-1}$ (Cremer, Pahl 1962).

Since the particles are attracted to each other in consequence of polarization of the neutral partner by the ion, the effective reaction cross-sections may be a multiple of the gas-kinetic cross-section. From the (classic) theoretical expression for this coefficient (α polarizability, v_{rel} relative velocity, μ reduced mass),

$$\gamma_{chem} = v_{rel}\ \pi\ b^2 \quad \text{with } b \text{ from } \frac{\mu}{2} v_{rel}^2 = \frac{2\alpha e^2}{b^4} ,$$

it is additionally found that the coefficient is independent of the temperature in this approximation.

At a distance $r \approx 10{,}000$ km from the nucleus, the reciprocal time scale of a reaction, if it is referred to an ion, is accordingly of the order of

$$x_r \cdot 10^{-1} \text{ to } x_r \cdot 10^{-2} \text{ sec}^{-1},$$

where x_r is the portion of volume of the reacting neutral partner. Time scales of the order of $10^2 - 10^3$ sec are obtained with $x_r = 10\%$, and $10^3 - 10^4$ sec, hence about an hour, at a distance from the nucleus of 30,000 km. If we refer the time scale to a particle of the neutral partner, the time scales become longer in the reciprocal ratio of the degree of ionization (hence by factors of the order of 100 to 10 between r = 10,000 and 100,000 km); moreover, the portion of volume x'_r of the ionized partner is to be substituted for x_r.

The following are examples of the reactions in question:

$$H_2O^+ + C_2H_2 \rightarrow CO^+ + CH_4 + 0.3 \text{ eV}$$
$$H_2^+ + CO_2 \rightarrow CO^+ + H_2O + 1.0 \text{ eV}$$
$$OH^+ + C_2H_2 \rightarrow CO^+ + CH_3 + 1.5 \text{ eV}$$
$$H_2O^+ + C_3H_4 \rightarrow CO^+ + C_2H_6 + \ ?$$

The differences between the binding energy of the diatomic molecules are greater than those of the ionization energies: CH has a value of about 3.5 ev, OH and H_2 both 4.5 ev; in contrast N_2 has 9.8 ev and CO 11.1 ev. The pertinent ionization energies are 11 ev for CH, 13.5 ev for OH, 15.4 ev for H_2, 15.6 ev for N_2, and 14.0 ev for CO. Hence the reactions in which CO or CO^+ arise from hydrogen compounds of C and O are generally exothermic. The average binding energy per H atom is 98 kcal for CH_4, 12 kcal for NH_3, and 109 kcal for H_2O (Gaydon 1947; 100 kcal = 4.3 ev).

This suggests the question of whether the CO^+ observed in the tails does not owe its origin predominantly to a chemical reaction. As is known, the observed time scales of the formation of structures consisting of CO^+ (envelopes and rays) led to the difficulty that both photoionization and charge transfer in the proton stream of solar corpuscular radiation yielded overly long time scales (cf. Section 3, charge transfer cross-section for CO of $3 \cdot 10^{-15}$ cm^2). That is to say, with the total production assumed here, even the ions formed by photoionization in the vicinity of the nucleus, at a distance of 10,000 or 20,000 km, would suffice to yield in point of number the observed ion stream of 10^{28} - 10^{29} sec^{-1}. A prerequisite for this is, of course, that both C and O be present largely in the form of hydrogen compounds (in this connection cfr. Donn and Urey 1957), so that chemical energy is gained by the formation of CO^+.

For instance, if a certain quantity of a class of molecules which reacts after photoionization were to be evaporated discontinuously from the surface the ionized fraction would react relatively rapidly, but the time scale of the reaction would increase outwards proportionally to r^2, while those of several competitive processes are either constant in the first approximation (thus photodissociation of the ion) or would increase outwards only in proportion to r. If one of the partners is already a product of a photodissociation, the conditions are somewhat more complicated; a further possibility, lastly, is that not the ionized but the neutral partner flows discontinuously from the surface.

Several models, on the basis of which these possibilities are discussed quantitatively, are given in what follows.

10. Models For The Formation of CO^+ By Chemical Reactions

Let us assume that the dependence of the density of a reaction partner (generally the neutral one) on r is known and that this density is only slightly dependent on the chemical reaction.

A simple case, for example, is that in which the neutral partner (let it be designated as B) is released from the surface of the cometary nucleus with a certain velocity v_B and in flowing outward dissociates with a certain probability β, say by photodissociation. Then the density is given by

$$n_B(r) = \frac{Q_B}{v_B r^2} e^{-\beta r / v_B} \qquad (20a)$$

Q_B is the number of particles B leaving the comet per sec and solid angle (about 10^{30} sec^{-1}).

Or we may assume that substance B itself only arises through photodissociation of a parent substance B_o. If in the simplest case we set the lifetime of B_o to equal that of B, we obtain the density

$$n_B(r) = \frac{Q_{B_o} \beta_d}{v_B^2 \, r} e^{-\beta r / v_B} \qquad (20b)$$

(β_d = probability that B_o dissociates to B, β = total dissociation probability of B_o and B).

For the other reaction partner A, which we conceive of as being ionized, the density is calculated under the following assumptions: A arises from A_o with the (constant) probability α_i, say by photodissociation. It is destroyed once by the chemical reaction,

$$A + B \rightarrow X + Y \qquad (X, \text{ for example, } CO^+)$$

with the probability $n_B\gamma$, or by other processes, e.g., photo processes the probability of which is to be set constant and equal to α. Let the total decay probability of A_o be set as equal to α_o. In the stationary case, if

$$N_A(r) = r^2 n_A(r) \qquad (5')$$

is the density per solid angle and cm along r, the following is valid:

$$v_A \frac{dN_A}{dr} = -N_A(\alpha + n_B\gamma) + N_{A_o}\alpha_i \qquad (21)$$

with

$$N_{A_o}(r) = \frac{Q_{A_o}}{v_A} e^{-\alpha_o r / v_A} \qquad (22)$$

and

$$N_A(0) = 0 \tag{23}$$

The differentiation between v_A and v_B takes into account the possibility that one of the two substances may leave the cometary nucleus explosively. Properly speaking, of course, the process would then be non-stationary, as indeed the processes occurring on the comet are largely non-stationary. Nevertheless, the stationary solutions describe the conditions in front of and behind a discontinuity arising from a stepwise change in mass outflow and moving outward with velocity v_A and v_B respectively. Let change in the velocities with radius r be ignored. The equation may be solved explicitly. However, the original differential equation is better suited for numerical evaluation than is the formal expression for the solution.

The equation should reflect the conditions in approximation up to a radius of about (50 - 100) $\cdot$ 10^3 km, beyond which the spherical geometry is increasingly disturbed by external influences such as pressure and magnetic effects of interplanetary matter.

Nine physical quantities were introduced in description of the model: the decay probabilities α_o, α, β; ionization probability α_i; chemical reaction rate γ; productions Q_A, Q_B (Q_{B_o} and β_d, respectively); and velocities v_A, v_B. Numerical calculation, in contrast, depends only on three dimensionless quantities:

$$p = \frac{Q_B \gamma}{v_B v_A r_o} \text{ and } \frac{Q_{B_o} \beta_d \gamma}{v_B^2 v_A}, \quad q = \frac{\alpha r_o}{v_A}, \quad q_o = \frac{\alpha_o r_o}{v_A} \quad \text{(respectively)} \tag{24a,b,c}$$

in which the radius unit was set as

$$r_o = \frac{v_B}{\beta} \tag{25}$$

The equation, rendered dimensionless, is

$$\frac{dF(x)}{dx} = - F(x) \left(q + p \cdot Di(x) \right) + e^{-q_o x} \tag{26}$$

in which

$$x = r/r_0 \tag{27}$$

and
$$Di(x) = e^{-x}/x^2 \qquad \text{Formula (20a)} \tag{28a}$$

and respectively
$$= e^{-x}/x \qquad \text{Formula (20b)} \tag{28b}$$

We have $N_A(r) = N_A(r_0 x) = \frac{Q_A \alpha_i}{v_A \alpha_0} q_0 \times F(x) = N^0 \times F(x)$ (29)

or
$$n_A(r) = \frac{Q_{A_0} \alpha_i}{v_A^2 r_0} \times \frac{F(x)}{x^2} = \frac{N^0}{r_0^2} \times \frac{F(x)}{x^2} \tag{30}$$

The production rate Prod (per sec solid angle and cm along r) of X = CO^+, as well as its density N_{CO^+} (per solid angle and cm along r), may be calculated from n_A and n_B:

$$\text{Prod} = N_A n_B \gamma = N^0 \times \frac{v_A}{r_0} \times p \cdot F(x) \cdot Di(x) \tag{31}$$
$$= N^0 \cdot \frac{v_A}{r_0} \times PROD(x)$$

$$N_{CO^+} = \frac{1}{v_A} \int_0^r N_A n_B \gamma \, dr = N^0 \int_0^{r/r_0} PROD(x)\, dx \tag{32}$$
$$= N^0 \times JNT(x)$$

and
$$n_{CO^+} = \frac{N^0}{r_0^2} \times \frac{JNT(x)}{x^2} \tag{33}$$

The number N_{CO^+} of CO^+ molecules in the sight line can be obtained for the head only if the distance s from the cometary nucleus is so small that the principal contributions come from regions ($r \lesssim 100{,}000$ km) in which the following model is still valid:

$$\mathcal{N}_{CO^+}(s) = \frac{N^0}{r_0} \times 2 \int_{s/r_0}^{\infty} JNT(x) \frac{dx}{x\sqrt{x^2 - s^2/r_0^2}} \tag{34}$$

The total CO^+ production (per sec) in our model is

$$4\pi Q_{CO^+} = 4\pi N^0 v_* \cdot JNT(\infty) \tag{35}$$

Each numerical model corresponds to a six-dimensional variety of physical models. Its behavior is difficult to survey in complete generality. Hence we shall confine ourselves to individual examples. We take the numerical values for photodissociation and photoionization probability from Table 1.

The calculation results are shown in Figures 2 to 9. Conversion is there made to dimension-bound quantities in conformity with the parameters indicated in the text. For the sake of completeness we give the computational parameters and conversion factors in Table 2. The total CO^+ production is also indicated.

Table 2

Model	Formula for n_B	p	q	q_0	r_0 (km)	N^0 (cm^{-1})	$4\pi Q_{CO^+}$ (sec^{-1})
1	(20a)	10	.5	.5	2×10^5	10^{24}	10^{30}
2	(20b)	5	1	1	2×10^5	10^{24}	0.75×10^{30}
3	(20a)	70	.1	.1	$.5 \times 10^5$	10^{22}	0.6×10^{29}
4	(20b)	70	.1	.1	$.5 \times 10^5$	10^{22}	0.8×10^{29}
5	(20a)	.2	10	10	5×10^5	2.5×10^{23}	2×10^{28}
6	(20b)	.2	10	10	5×10^5	2.5×10^{23}	0.5×10^{28}
7	(20a)	.1	1	1	2×10^5	2×10^{22}	1.3×10^{28}
8	(20b)	.1	1	1	2×10^5	2×10^{22}	0.5×10^{28}

First model.

A, heavier molecule ion, e.g., $C_2H_2^+$, $C_2H_4^+$, $C_2H_6^+$, HCN^+

$$\alpha = \alpha_o = ½ \cdot 10^{-5}\ \text{sec}^{-1}\ \text{(photodissociation)}$$

$$\alpha_i = ½ \cdot 10^{-6}\ \text{sec}^{-1}\ \text{(photoionization of parent substance } A_o\text{)}$$

$$v_A = 1\ \text{km/sec}$$

B, e.g., H_2O

$$\beta = 2 \cdot 10^{-5}\ \text{sec}^{-1}\ \text{(photodissociation of } H_2O$$

$$v_B = 4\ \text{km/sec (explosive)}$$

n_B in accordance with formula (20a)

$\frac{Q_B}{v_B} = 10^{25}$ particles/cm • solid angle.

With a chemical reaction rate of

$$\gamma = 10^{-9}\ \text{cm}^3/\text{sec}$$

and a production of A_o molecules of

$$\frac{Q_{A_o}}{v_A} = 10^{25}\ \text{particles/cm} \cdot \text{solid angle,}$$

the differential equation yields

$$n_{CO^+} = 5 \cdot 10^3 \cdot \frac{10^5\ \text{km}}{r}\ \text{cm}^{-3}$$

for small radii. Further outward ($r \gtrsim 4 \cdot 10^5$ km), the CO^+ density would decrease as

$$n_{CO^+} = 10^4 \cdot \left\{\frac{10^5\ \text{km}}{r}\right\}^2\ \text{cm}^{-3}.$$

It should be noted that Q_B/v_B and γ enter into the density of CO^+ only in the combination $\gamma Q_B/v_B$. The prerequisite that the density of H_2O be little affected by the chemical reaction, i.e., $\beta_{chem} = n_A\gamma << \beta$, is met insofar as the production of A_o is $Q_{A_o} < 16^{31}$ particles/sec • solid angle.

For observations of processes in the vicinity of the nucleus, say at a distance s from the nucleus, the densities of CO^+ are decisive up to about triple the distance, 3s. The time scale with which sudden eruptions from the cometary nucleus become visible is determined by the time it takes the substance to reach the decisive regions, hence for observations at a distance of $s = 20{,}000$ km from the nucleus about $t = 3s/v_B = 15 \cdot 10^3$ sec ≈ 4 h.

Second model.

The conditions are very similar if one assumes for the reaction partner B a substance which itself is the product of a photodissociation; that is, if one evaluates n_B in accordance with formula (20b), e.g., in reactions with the radical OH. Since n_B now decreases less intensively with r than in the preceding model (in proportion to r^{-1} rather than r^2), the formation of CO^+ is less concentrated toward the nucleus. However, the solutions show that the time it takes for eruptions to become visible is virtually the same. The regions which are decisive for the number of CO^+ ions in the sight line extend about 10 to 20% further outward than with the preceding model. Because of the large radii within which CO^+ is for the most part formed, the first two models seem to agree poorly with the actual conditions.

Third model.

If one assumes that reaction partner B (e.g., H_2O) is produced stationarily and flows outward at a velocity

$$v_B = 1 \text{ km/sec},$$

while the parent substance A of the charged reaction partner A is produced in a sudden eruption at

$$v_A = 3 \text{ km/sec},$$

the production of CO^+ is more strongly concentrated on the nucleus than in the two preceding models. (In the model calculated by us we set $\gamma Q_B/v_B \approx$ $\approx 10^{17} \cdot \text{cm}^2/\text{sec} \cdot$ solid angle; hence Q_B is assumed to be twice as great as in the first model; the dissociation probabilities are the same as in the first and second models).

The radius within which half the total CO^+ is formed is about 60,000 km, while it was about 10,000 km in the first model. The time t after which a sudden eruption becomes visible at distance s from the nucleus, is nevertheless again given by the geometry:

$$t = \frac{3s}{\mathrm{Max}\ (v_A,\ v_B)}$$

and is of the order of several hours for distances s of some 10^4 km.

The fourth model, in which reaction partner B (OH) results from B (H_2O) through photodissociation and for which the same parameters are used as in the third model, is less concentrated toward the nucleus and thus is intermediate between the first and third models.

Fifth model.

Still more heavily nucleus-concentrated are the last four models, in which ionized H_2O reacts with a heavier molecule. The fifth model is based on the following parameters:

$A = H_2O^+$, B heavier molecule, n_B in accordance with formula (20a)

$\alpha = \alpha_o = 2 \cdot 10^{-5}\ \mathrm{sec}^{-1}$ (photodissociation of H_2O)

$\alpha_i = \frac{1}{2} \cdot 10^{-6}\ \mathrm{sec}^{-1}$ (photoionization of H_2O)

$v_A = 1$ km/sec

$$\frac{Q_{A_o}}{v_A} = 10^{24}\ \frac{\text{particles}}{\text{cm solid angle}}$$

$\beta = \frac{1}{2} \cdot 10^{-5}\ \mathrm{sec}^{-1}$

$v_B = 2.5$ km/sec

$$\frac{\gamma Q_B}{v_B} = 10^{15}\ \frac{\text{particles}}{\text{cm solid angle}} \cdot \frac{\text{cm}^3}{\text{sec}}$$

The total CO^+ production is lower for all four models than with the first models and is of the order of magnitude of 10^{28} molecules/sec. Half the CO^+ in the fifth model is already formed within a radius of 22,000 km.

The sixth model differs from the fifth only in that formula (20b) is used for n_B. Hence it is assumed that the reaction partner of the H_2O^+ is itself formed by photodissociation. The cometary atmosphere is thereby enlarged somewhat in comparison with the fifth model. Half the CO^+ is formed within a radius of 30,000 km.

Seventh and Eighth models.

The last two models are perhaps the most realistic ones; they differ from the preceding ones in that we have set

$$v_A = 4 \frac{km}{sec} \qquad v_B = 1 \frac{km}{sec},$$

that is, the H_2O ion has the greater velocity. The same values are assumed for α, α_o, α_i, and β as in the fifth model. $Q_A/v_A = 0.8 \cdot 10^{24}$ (cm $\cdot$ solid angle)$^{-1^o}$, $\gamma Q_B/v_B = 0.8 \cdot 10^{15}$ cm^2/sec. In the seventh model n_B is represented by formula (20a) and in the eighth model by formula (20b). The radii within which half the CO^+ is formed are respectively 26,000 km and 70,000 km.

Reactions with OH^+ or H_2^+ are not included in our models, since in this case the ionized reaction partner arises in a more complicated way than is assumed in our calculation.

Nevertheless it is to be expected that an additional photodissociation in the formation of the ion changes the picture no more greatly than does an additional photodissociation for the neutral partner if formula (20b) rather than formula (20a) is used for n_B. Thus in reactions with OH^+ the CO production extends over a somewhat larger region than in the case of the models with H_2O^+ calculated here.

Since it may be assumed that with very small radii the velocity of the molecule is often substantially smaller than 1 km/sec, it is conceivable that a first photodissociation takes place in the immediate environment of the cometary nucleus and that at the distances in which we are interested ($r \approx 10,000$ km) the dissociation products behave as if they have been evaporated directly from the nucleus. The density in accordance with formula (20a) would be the one to assume for such substances. Observations of neutral molecules support this conception (Wurm 1961b).